Particles, atoms, and crystals 1

The hydrogen atom and center-of-mass coordinates

Modern physics for engineers

David Miller

The hydrogen atom

- This problem can be solved essentially exactly
  - using Schrödinger's equation
    - and standard mathematical approaches
      - though the detail takes some time
- We introduce the overall approach briefly
  - avoiding most of the algebra
    - showing the core ideas and main results
      - which can be understood relatively simply

The hydrogen atom – a “two particle” problem

The hydrogen atom

The hydrogen atom consists of

- one electron
  - mass $m_e \simeq 9.109\ 382\ 91 \times 10^{-31}$ kg
  - charge -e where $e \simeq 1.602\,176\,565 \times 10^{-19}$ C
- and one proton
  - mass $m_p \simeq 1.672\ 621\ 777 \times 10^{-27}$ kg
  - charge $+e$

Solving for its quantum mechanical behavior

- involves solving for two quantum mechanical particles at once

Hydrogen atom solutions

Classically, we think of a hydrogen atom as

- a negatively charged electron orbiting
- a positively charged proton
  - as in the Bohr model

That classical model suggests a way of separating the problem into two

- which is to use
  - center-of-mass coordinates

Center of mass separation

Separation into two problems

Our two separate problems become

- an atom particle

  with total mass that is the sum of the electron and proton masses

  that can be described with its own Schrödinger equation for a particle of that mass

- an electron and a proton both orbiting round the "center of mass"

The “center of mass” approach

Just like the classical problem
- in the electron-proton “orbit”
  - the electron does not quite orbit the proton

Instead, each of them is orbiting around the “center of mass”
- very nearly at the proton position
  - but not quite

Center of mass coordinates

Center of mass separation

- We formally transform to "center of mass" coordinates
  - The center of mass is like the balance point of a seesaw
    - with the electron at one end and the proton at the other

Center of mass separation

Because the electron is much lighter
- by a factor of ~ 1836
  - than the proton
    - this center of mass
      - is very nearly but not quite at the proton position

We can essentially think the electron is orbiting round the proton
- but with a “reduced mass” that incorporates this center of mass correction

Center of mass separation

So we construct a Schrödinger equation for the "electron"

formally in terms of the distance between the electron and the proton

and using the

"reduced mass" μ

where $$\frac{1}{\mu} = \frac{1}{m_{electron}} + \frac{1}{m_{proton}}$$

which is slightly less than the electron mass

$$\mu \simeq 9.104\,424\,485 \times 10^{-31} \text{ kg}$$

Potential energy

The potential energy we use

comes from the Coulomb attraction of the electron and proton

which is an inverse square force $\propto 1/r^2$

where r is the distance between the particles

Integrating the force times distance

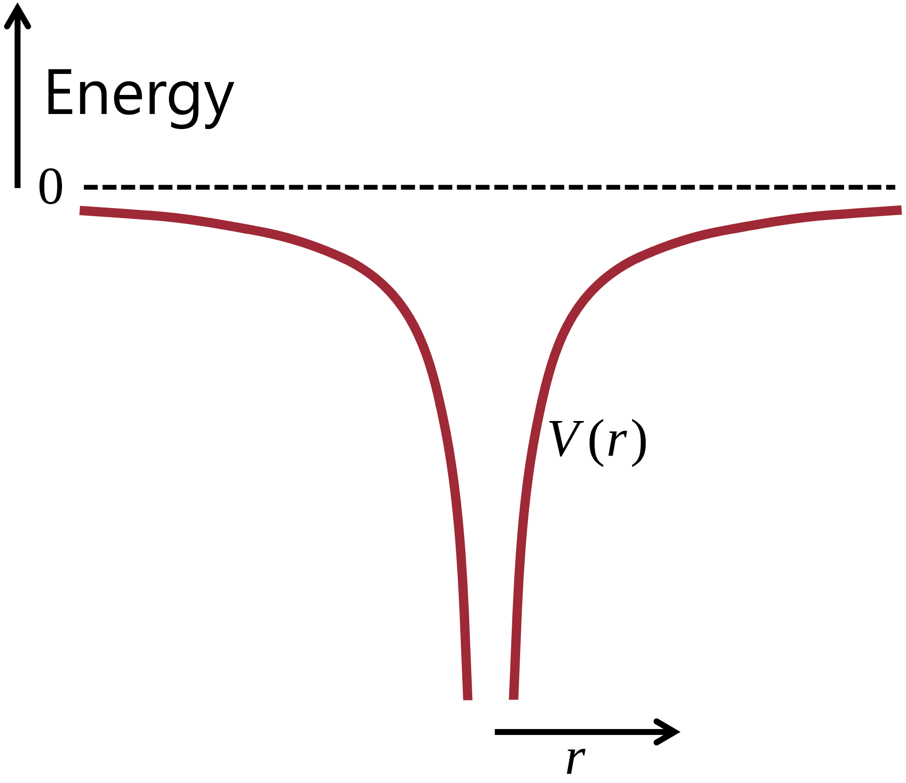
starting from the particles infinitely far apart

gives the potential energy

$$V(r) = -\frac{e^2}{4\pi\varepsilon_o r} \qquad \varepsilon_o = \frac{1}{4\pi \times 10^{-7} c^2} \simeq 8.854\,187\,817\ldots \times 10^{-12} \text{ F/m}$$

Potential energy

Note $V(r) = -\frac{e^2}{4\pi\varepsilon_o r}$ is negative



It takes energy to pull the electron and proton apart

and we are formally using the energy when they are arbitrarily far apart

as the zero of potential energy here

Particles, atoms, and crystals 1

The hydrogen atom solutions and angular behavior

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The Schrödinger equation for the hydrogen atom

Schrödinger equation for hydrogen states

With these center-of-mass coordinates

and the Coulomb potential energy

the Schrödinger equation for the "electron"

technically for the relative motion wavefunction

$U(\mathbf{r})$ of the electron and proton

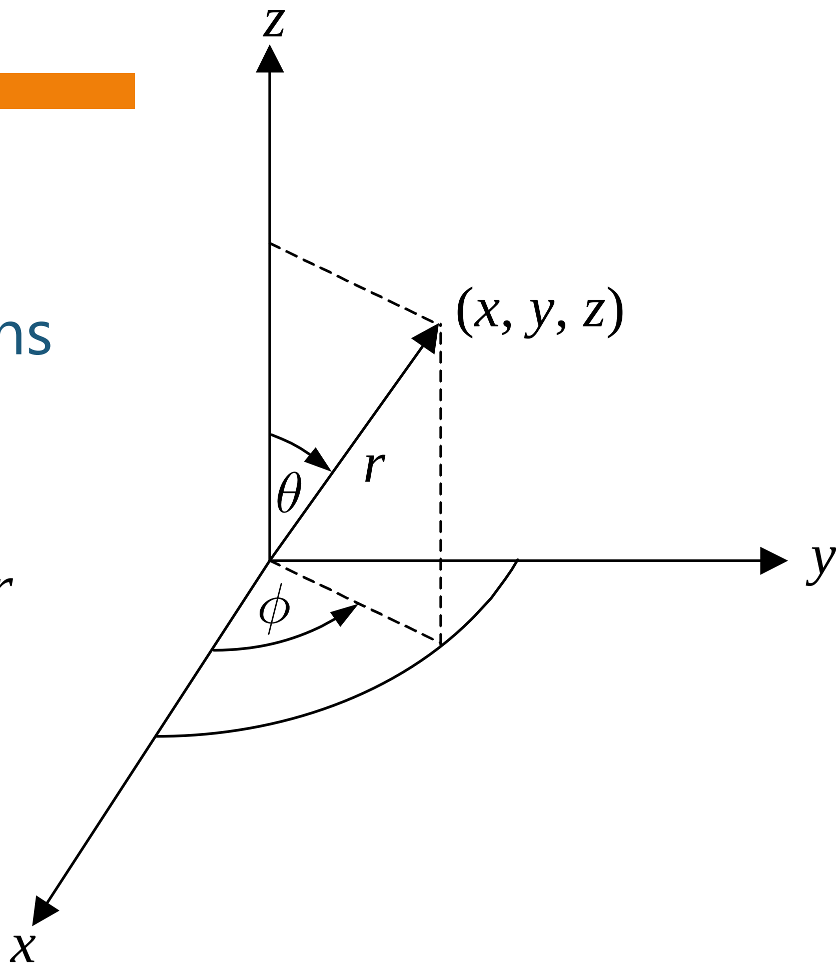
becomes

$$\left(\frac{-\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_o r}\right)U(\mathbf{r}) = EU(\mathbf{r})$$

Spherical polar coordinates

Because the potential is
- spherically symmetric
  - that is, the same in all directions

this problem is best solved using
- a spherical coordinate system
  - with a radius from the center, r
    - and two angles
      - θ is the polar angle, and
      - ϕ is the azimuthal angle



Hydrogen atom solutions

Because the potential energy $V(r) = -\frac{e^2}{4\pi\varepsilon_o r}$

does not depend on angle, but only on separation r

what is called a "central potential"

we can separate the solutions into

- an angular function $Y(\theta,\phi)$
- a radial function $R(r)$

so the total wavefunction is

$$U(\mathbf{r}) = R(r)Y(\theta,\phi)$$

Spherical harmonics

Spherical harmonics

The solutions for the angular part $Y(\theta,\phi)$

are "spherical harmonics"

Formally, these are of the form

$$Y_{lm}(\theta,\phi) \propto P_l^m(\cos\theta)\exp(im\phi)$$

where $P_l^m(x)$ are the

associated Legendre functions

which are real

so the only complex part is from the exponential

Spherical harmonics

The spherical harmonics are indexed by integers l and m

$$Y_{lm}(\theta,\phi) \propto P_l^m(\cos\theta)\exp(im\phi)$$

These functions must have the property of

coming back to where they started if we go round in a circle

so $Y(\theta,\phi) = Y(\theta+2\pi,\phi) = Y(\theta,\phi+2\pi)$

Because $\cos\theta$ is periodic in this way

$P_l^m(\cos\theta)$ automatically is also

Spherical harmonics

In $Y_{lm}(\theta,\phi) \propto P_l^m(\cos\theta)\exp(im\phi)$

for $\exp(im\phi)$ to be periodic in this way

$$\exp(im\phi) = \exp[im(\phi+2\pi)] = \exp(2\pi im)\exp(im\phi)$$

which means m must be an integer

The detailed solution also requires l is an integer

specifically

$$l = 0, 1, 2, 3, \ldots$$

and m must lie between $-l$ and $+l$

$$-l \le m \le l$$

Hydrogen atom quantum numbers

There are three quantum numbers for the hydrogen atom

- n is the principal quantum number
- l is the orbital quantum number
  - or the angular momentum quantum number
  - or the azimuthal quantum number
- m is the magnetic quantum number

Particles, atoms, and crystals 1

Spherical harmonics for a classical problem

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Spherical harmonics and a classical problem

Spherical harmonics can arise in classical problems

- such as the vibration modes of a spherical shell

Classical problems only have real amplitudes

- so we use two sets of spherical harmonic functions
  - one in which we replace the $\exp(im\phi)$ with $\cos m\phi$
    - which are the real part of our complex spherical harmonic functions
  - another in which we replace the $\exp(im\phi)$ with $\sin m\phi$
    - which are the imaginary part of our complex spherical harmonic functions

Spherical harmonics and a classical problem

These two different sets of spherical harmonic functions

are really just the same functions but rotated by $90°/m$

in the azimuthal (equatorial) plane

In the classical case, instead of letting m run from $-l$ to $+l$

we simply choose it to be zero or positive

and use both the cosine and sine forms

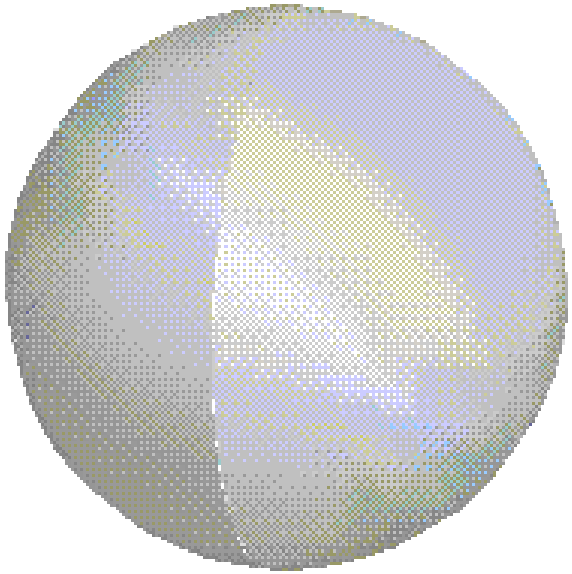
When spherical harmonic functions are plotted

even in discussions of quantum mechanical problems

such as the hydrogen atom

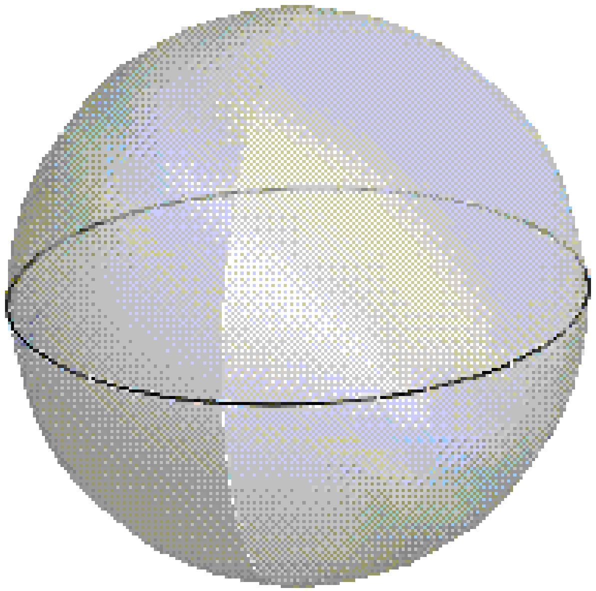
it is these real forms that are shown

Oscillating modes for spherical shell



$l = 0$
$m = 0$

Oscillating modes for spherical shell



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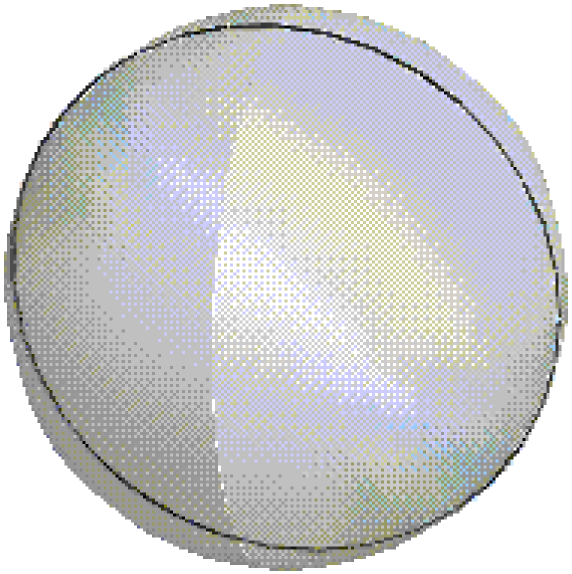
Oscillating modes for spherical shell



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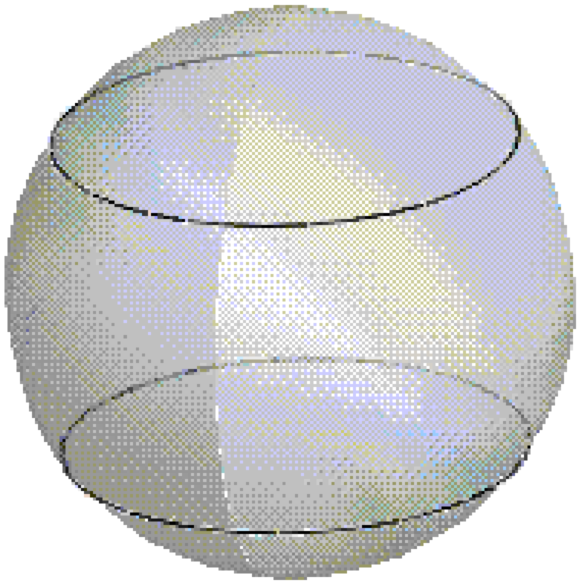
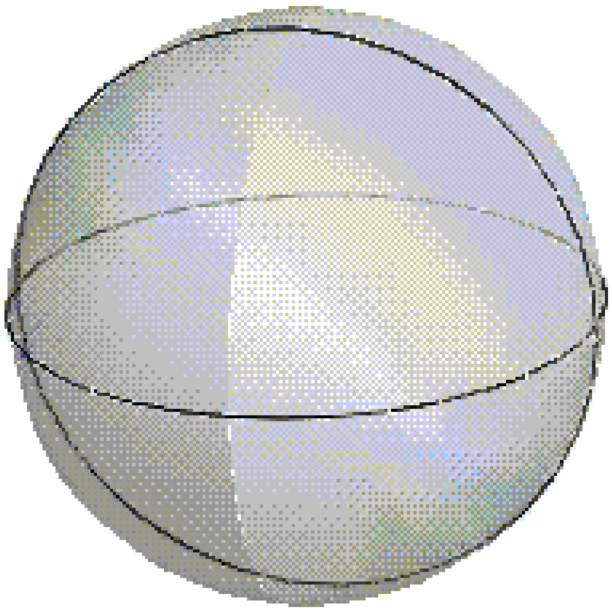


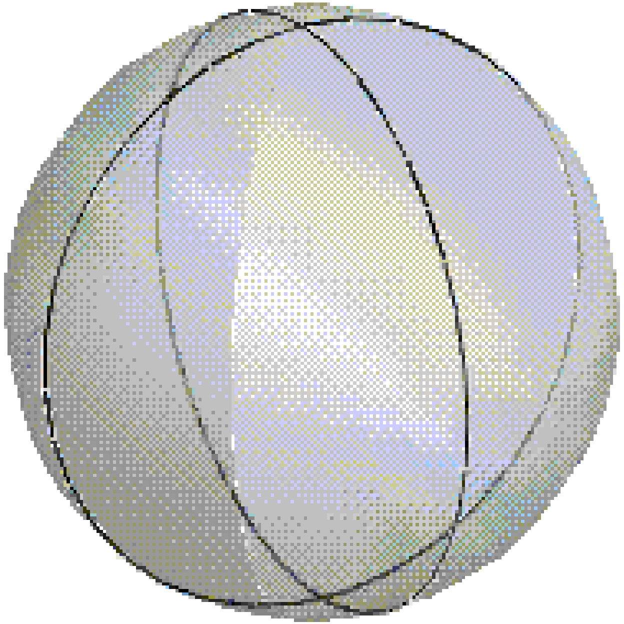
$l = 2$
$m = 0$

Oscillating modes for spherical shell



$l = 2$
$m = 1$

Oscillating modes for spherical shell



$l = 2$
$m = 2$

Constructing spherical harmonics for a shell

The lowest solution

$$l = 0,\ m = 0$$

- is the "breathing" mode
  - The spherical shell expands and contracts periodically

For all other solutions

- there are one or more nodal circles on the sphere
  - A nodal circle is one that is unchanged in that particular oscillating mode

Constructing spherical harmonics for a shell

Note the following rules for the spherical shell modes

- the surfaces on opposite sides of a nodal circle oscillate in opposite directions
- the total number of nodal circles is equal to l
- the number of nodal circles passing through the poles is $|m|$, and they divide the sphere equally in the azimuthal angle ϕ (i.e., round the equator)
- the remaining nodal circles are either equatorial or parallel to the equator

  symmetrically distributed between the top and bottom halves of the sphere

Particles, atoms, and crystals 1

Polar plots of spherical harmonics

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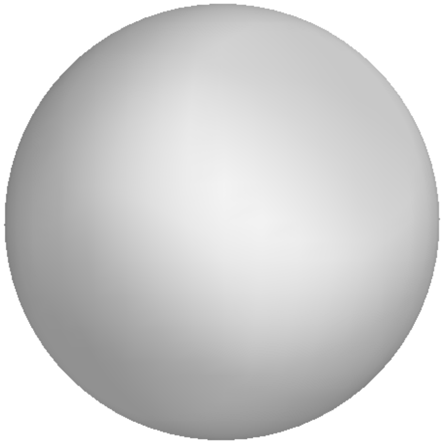
Spherical harmonics

We can formally also plot the spherical harmonic in a parametric plot

- where the distance from the center at a given angle
  - represents the magnitude of amplitude of the spherical harmonic



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Spherical harmonics

We can formally also plot the spherical harmonic in a parametric plot

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    - Adjacent "lobes" have opposite signs

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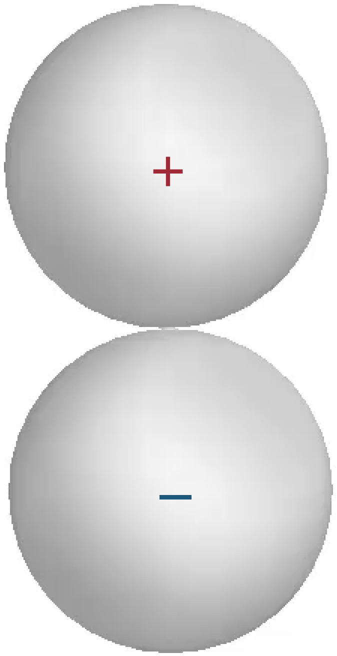

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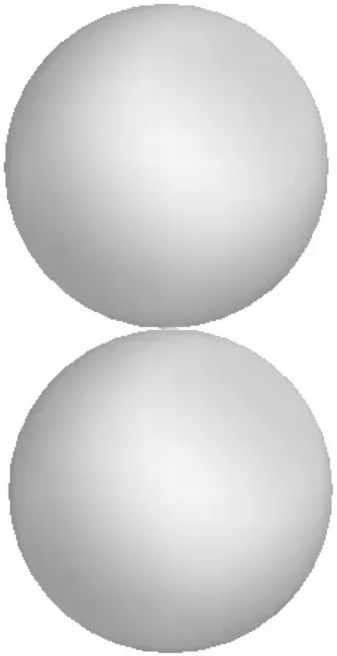

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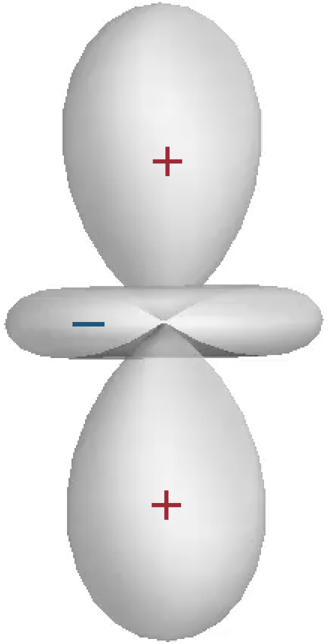

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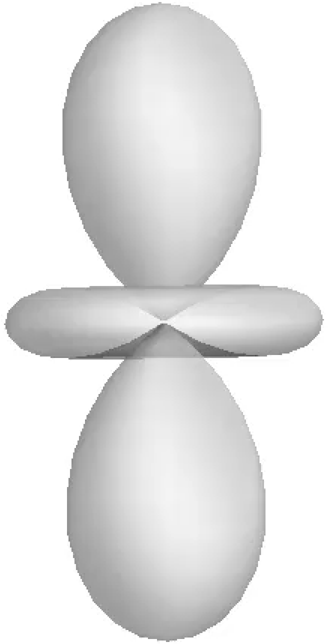

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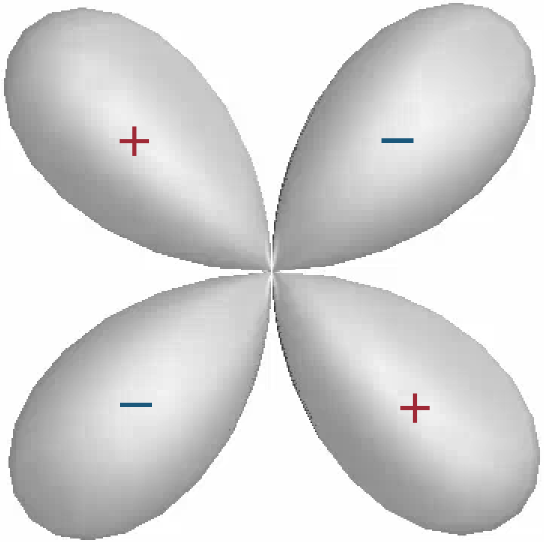

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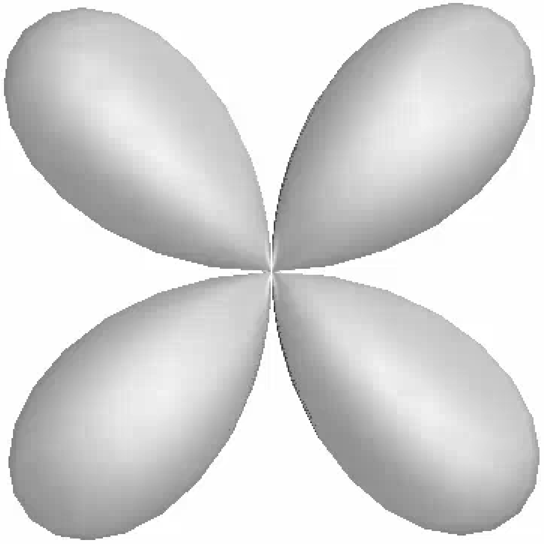

Particles, atoms, and crystals 1

Spherical harmonics and atomic orbitals

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Spherical harmonics and atomic orbitals

- Though we have not yet solved the hydrogen atom problem
  - if we did that
    - we would get spherical harmonic angular shapes of the orbitals
- Though other atoms are more complicated than the hydrogen atom
  - as a first approximation
    - their orbitals have the same angular form
      - and we use the same notation

“s, p, d, f” notation

In the use of the spherical harmonics in the solution of the hydrogen atom problem

different values of l give rise to

different sets of spectral lines from hydrogen

identified empirically in the 19th century

Spectroscopists identified groups of lines called

- “sharp” (s)
- “principal” (p)
- “diffuse” (d), and
- “fundamental” (f)

"s, p, d, f" notation

Each of these is now identified with specific values of l

Now we also alphabetically extend to higher l values

l	0	1	2	3	4	5
notation	s	p	d	f	g	h

It is convenient that

the "s" wavefunctions are all spherically symmetric

even though the "s" of the notation originally

had nothing to do with spherical symmetry

We only need s, p, d, and f to describe ground states of atoms

Angular momentum and spherical harmonics

Bohr's early model of the hydrogen atom

- proposed angular momentum was quantized in units of $\hbar$
- A related idea survives
  - in the Schrödinger equation solutions
    - where the orbitals have an angular momentum
      - around the polar (z) axis of an amount $m\hbar$

Magnetic quantum number

m is called the magnetic quantum number because

- the levels of different m split to different energies with applied magnetic field
  - the "Zeeman" effect

A point "electron" in orbits of different angular momentum

- would show different energies because
  - such an orbiting "point particle" is a current loop

Note m is the quantum number for angular momentum

- not the "principal quantum number" n
  - and m can be zero also